



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 457 471 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
29.01.1997 Bulletin 1997/05

(51) Int Cl.⁶: **C08L 27/06, C08K 3/00**
// (C08K3/00, 3:16, 3:34)

(21) Application number: **91304066.3**

(22) Date of filing: **07.05.1991**

(54) **Polymer stabilizer and polymer composition stabilized therewith**
Polymerstabilisator und damit stabilisierte Polymerzusammensetzung
Stabilisateur pour polymères et composition de polymères ainsi stabilisée

(84) Designated Contracting States:
BE DE FR GB IT NL

(30) Priority: **18.05.1990 US 525443**

(43) Date of publication of application:
21.11.1991 Bulletin 1991/47

(73) Proprietor: **WITCO CORPORATION**
New York New York 10022 (US)

(72) Inventors:
• **Bae, Kook-Jin**
East Northport, New York 11731 (US)
• **Martin, Curtis R.**
Butler, New Jersey 07405 (US)

(74) Representative: **Harrison, David Christopher et al**
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(56) References cited:
• **World Patent Index Latest, Derwent Publications Ltd, London, GB; AN 83-749789**
• **World Patent Index Latest, Derwent Publications Ltd, London, GB; AN 90-196099**
• **World Patent Index Latest, Derwent Publications Ltd, London, GB; AN 88-187379**
• **World Patent Index Latest, Derwent Publications Ltd, London, GB; AN 83-822923**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

EP 0 457 471 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

The present invention relates to stabilizer compositions for polyvinyl chloride resins and to polyvinyl chloride resin compositions having improved resistance to degradation caused by heat. More particularly, the present invention relates to improved sodium perchlorate stabilizer compositions and their use in polyvinyl chloride resin compositions. Although capable of a variety of uses, this invention finds advantageously utility in providing improved long term stability at moderate temperatures to motor vehicle components shaped from polyvinyl chloride resin compositions, especially where the polyvinyl chloride resin compositions are used in combination with urethane.

The problem of imparting to polyvinyl chloride a sufficient heat processing stability at temperatures in which the polymer becomes sufficiently fluid or softened to permit shaping is of course of long standing, and has been satisfactorily resolved by addition to the polymer of various combinations of known heat stabilizers. At these temperatures, the resin can degrade, liberating hydrogen chloride, and discolor, become brittle, and stick to the equipment. These problems are overcome by combining with the polymer before heat processing or during heat processing one or more of the well established and successful conventional heat stabilizers, such as, for example, the well known organotin stabilizers and/or barium-cadmium or barium-zinc salt stabilizers.

Although the well established and successful conventional heat stabilizers provide effective stabilization to the polymer at elevated heat processing temperatures during standard processing, they may not provide effective stabilization to the polymer at lower more moderate temperatures after such heat processing. For example, protection against discoloration at moderate temperatures over long periods is a particular problem with motor vehicle components shaped from polyvinyl chloride resin compositions despite such compositions having contained conventional heat stabilizers during their heat processing. Depending upon their location in the vehicle, these components may be exposed to varied amounts of light, and also different rather high (above atmospheric) temperatures in use, and these differences can degrade motor vehicle components at differing rates. Additionally, when polyvinyl chloride resin compositions are associated with a polyurethane foam backing, e.g. automobile instrument panels, glove compartments, door handles, arm and head rests, the amine from the urethane can contribute to discoloration of the polyvinyl chloride resin composition.

A number of stabilizing systems have been proposed for imparting polyvinyl chloride resin articles molded with a polyurethane foam backing with resistance to deterioration from exposure to long term moderate heat and from exposure to an amine from urethane. For example, the art has recognized the use of perchlorate salts in polyvinyl chloride resin stabilization and in particular in stabilizing polyvinyl chloride that is used in contact with polyurethane foam or plastic. EP-A-212559 discloses polyvinyl chloride resin stabilizer compositions comprising a 2, 2, 6, 6-tetramethyl piperidinyll compound and an ammonium or metal perchlorate. This publication also discloses the use of such stabilizer compositions for polyvinyl chloride resin articles molded with polyurethane foam backing.

US-A 4,861,816 discloses polyvinyl chloride compositions containing a stabilizer mixture of certain barium/zinc carboxylic acid salts and a metal perchlorate and/or Perchlorate ion type hydrotalcite. According to this patent the perchlorate and perchlorate ion type hydrotalcite compound give excellent amine resistance particularly to urethane attached polyvinyl chloride sheets.

Perchlorates, however, are dangerous oxidizing materials and great care is needed in using them safely. Due to this hazard there may exist some reluctance in the industry to utilize perchlorate salts for polyvinyl chloride resin stabilization. Accordingly, there exists a need for a perchlorate stabilizer composition of reduced hazard level. Additionally, there exists a need for improved perchlorate salt stabilizer compositions for polyvinyl chloride resin compositions exposed to long term, above ambient temperatures, especially when such compositions are in contact with urethane.

Accordingly, a general object of the present invention is to provide an improved perchlorate salt stabilizer composition.

It is another object of the present invention to provide a perchlorate salt stabilizer composition of reduced hazard level.

The Derwent Abstract of JP-A-58122951 discloses a stabilized resin composition which has A) a halogen-containing resin, which may be polyvinyl chloride, B) at least one metal carboxylate salt, C) a calcium silicate material and D) a salt of an oxyhalogeno-acid, and sodium and perchlorate are listed.

It is an object of the present invention to provide for stabilizing halogen-containing organic or polymer resin compositions particularly those in contact with polyurethane, against long term moderate temperature degradation. For this purpose, the inventive composition includes a primary heat stabilizer to provide stability at processing temperatures of 150-205°C, and 0.1 to 10 parts by weight, based on the resin, of a secondary stabilizer which is a blend of sodium perchlorate hydrate and calcium silicate. The function of the latter is to provide improved long term heat stability to a polyvinyl chloride resin containing the conventional (primary) heat stabilizer. Additionally, it has been found that a combination of a solution of sodium perchlorate in water with calcium silicate and a non-absorbing diluent powder such as calcium carbonate provides a free-flowing powder composition of reduced hazard level. Improved resistance to deterioration of motor vehicle components made of polyvinyl chloride resin compositions is obtained by combining with

the polyvinyl chloride resin at least one conventional heat stabilizer and a mixture of sodium perchlorate and calcium silicate in a sufficient amount to provide, after formation of a motor vehicle component, resistance to deterioration at moderate temperatures.

The polymers or resins which may be stabilized by practice of this invention may be halogen-containing organic polymers typically those which contain chlorine atoms bonded to the polymer chain. These polymers may be homopolymers including polyvinyl chloride-type polymers, e.g. polyvinyl chloride. These polymers may also include copolymers formed by the copolymerization of vinyl chloride with other ethylenically unsaturated monomers. Ethylenically unsaturated monomers may be compounds which contain polymerizable carbon-to-carbon double bonds and may include alpha olefins such as ethylene, propylene and 1-hexene; acrylates, such as acrylic acid, ethyl acrylate, acrylonitrile; vinyl monomers, such as styrene, vinyl acetate; and/or maleates, such as maleic acid, maleic anhydride, maleic esters. For convenience, reference will be hereinafter made to vinyl chloride polymers.

The stabilizer combinations of this invention have applicability to both unplasticized or rigid polyvinyl chloride resins as well as plasticized polyvinyl chloride resins. The present invention has particular applicability to those polyvinyl resins used in association with urethane products including, but not limited to, polyurethane foams and plastics. The rigid polyvinyl chloride resins are defined as those containing at most about 10 percent plasticizer. Plasticized resins contain at least 10 percent plasticizer and can contain as much as 50 to 60 percent plasticizer according to the degree of plasticization desired. When plasticizers are to be employed, they may be incorporated into polyvinyl resins using conventional means. Conventional plasticizers can be used, such as dioctylphthalate, dioctylsebacate and tricresyl phosphate. Additionally, it is possible to use epoxy plasticizers and polyester plasticizers.

The vinyl chloride polymers may also include other conventional additives and ingredients. These additives and ingredients include, but are not limited to, impact modifiers, pigments and/or fillers, lubricants.

The preparation of the stabilized polymer composition is accomplished by conventional procedures. The selected stabilizer combination along with the desired compound and ingredients such as colors, lubricants and antistatic agents, as may be needed, is blended with the polymer being stabilized, using, for instance, plastics mixing rollers at a temperature at which the mix is fluid and thorough blending facilitated, typically at from 120° to 180°C for time sufficient to form a homogeneous sheet, 5 minutes, usually. After the mass is formed, it is sheeted off in the usual way.

A sufficient amount of a conventional heat stabilizer or of a combination of conventional heat stabilizers is used to provide resistance to the polyvinyl resin from deterioration and physical properties during heat processing, including, for example, discoloration, reduction in melt viscosity and embrittlement. The conventional heat stabilizers include, but are not limited to conventional organo metallic stabilizers such as the known organotin mercaptides, organotin sulfides and organotin carboxylates and mixtures thereof, and the known metal salt stabilizers such as barium salts, zinc salts and mixtures thereof. The conventional stabilizers are normally used in an amount of 0.01 to 10 percent by weight of the resin and more preferably the conventional stabilizers are used in an amount of 0.1 to 5 percent by weight of the resin.

Specific examples of useful organotin stabilizers include alkyl mercaptides such as monomethyltin tris (isooctylthioglycolate), dimethyltin bis (isooctylthioglycolate), monomethyltin tris (2-ethylhexylthioglycolate), dimethyltin bis (2-ethylhexylthioglycolate), monobutyltin tris (isooctylthioglycolate), dibutyltin bis (isooctylthioglycolate), monobutyltin tris (2-ethylhexylthioglycolate), dibutyltin bis (2-ethylhexylthioglycolate), monomethyltin tris (mercaptoethylallate), dimethyltin bis (mercaptoethylallate), dibutyltin bis (mercaptoethylallate), monobutyltin tris (mercaptoethylaurate), dibutyltin bis (mercaptoethylaurate), monomethyltin bis (isooctyl 3-mercaptopropionate), dimethyltin bis (isooctyl 3-mercaptopropionate), monobutyltin tris (isooctyl 3-mercaptopropionate) and dibutyltin bis (isooctyl 3-mercaptopropionate); alkyltin sulfides such as monomethyltin sulfide, dimethyltin sulfide, monobutyltin sulfide and dibutyltin sulfide; alkyltin carboxylates such as dimethyltin dilaurate, dibutyltin dilaurate, dibutyltin dioctanoate, dibutyltin didecanoate, dibutyltin neodecanoate, dibutyltin dilaurate, dibutyltin ditallate, dioctyltin maleate, dibutyltin and bis (dodecyl maleate); and mixtures thereof.

Specific examples of useful metal salt stabilizers include barium di(nonylphenolate), barium di(nonyl-o-cresolate), barium laurate, barium ricinoleate, barium myristate, barium benzoate, barium oxalate, barium malonate, barium maleate, barium tartrate, barium p-tert-butylbenzoate, barium succinate, barium glutarate, barium adipate, barium pimelate, barium suberate, barium azelate and barium sebacate, cadmium-2-ethylhexoate, cadmium laurate, cadmium stearate, cadmium naphthenate, cadmium benzoate, cadmium epoxystearate, cadmium myristate, cadmium p-tert-butylbenzoate, zinc laurate, zinc oxalate, zinc malonate, zinc maleate, zinc tartrate, zinc benzoate, zinc p-tert-butylbenzoate, zinc succinate, zinc adipate, zinc malate and zinc stearate. Additionally, mixtures of the foregoing and/or other known metal salt stabilizers can be used. For example, a 99:1 by weight ratio blend of barium benzoate and zinc laurate has been found useful as has a 6:1 by weight blend of barium stearate and zinc laurate.

In addition to the conventional heat stabilizers, there can also be added conventional antioxidants such as phenolic antioxidants normally used in an amount of 0.01-10 percent, and more typically in an amount of 0.1 to 5 percent by weight of the weight of the conventional heat stabilizer. Additionally, conventional epoxy compounds such as epoxidized soy bean oil can be used in amounts of 0.01-10 percent by weight of the polymer.

In accordance with the present invention, in addition to the conventional heat stabilizer(s) and additives, a sufficient amount of a composition comprising sodium perchlorate hydrate and calcium silicate is used to improve the resistance of the synthetic polymer to deterioration and physical properties from long term moderate heat exposure such as that experienced by motor vehicle components in use.

5 The sodium perchlorate/calcium silicate stabilizer composition can be prepared by combining a solution of sodium perchlorate in water (approximately 60 percent or greater by weight sodium perchlorate) such as that commercially available from Kerr-McGee Chemical Corporation, with calcium silicate such as the synthetic amorphous calcium silicate sold by the J.M. Huber Corporation under the trade designation Hubersorb 600 which has an average particle size according to the Coulter counter method of approximately 3.2 micrometers. It has been found that calcium silicate
10 when used in combination with the sodium perchlorate solution not only provides improved long term heat stability compared to comparable use of sodium perchlorate alone, but also is able to absorb the water in the sodium perchlorate solution and provide a sodium perchlorate stabilizer composition which is relatively easy to handle and of reduced hazard level. Preferably, the sodium perchlorate/calcium silicate combination also contains a non-absorbing diluent powder such as calcium carbonate to improve the compositions flowability. In this regard, calcium carbonate commercially available by Thomson Weinman Company under the trade name Atomite has been used. Other non-absorbing
15 diluent powders include zeolites, silica, alumina, PVC resins and barium sulfate.

The sodium perchlorate/calcium silicate compositions of the present invention in general include 10 to 30 percent by weight of 60 to 75 percent aqueous sodium perchlorate monohydrate, 30 to 50 percent by weight of calcium silicate, and 30 to 50 percent by weight of calcium carbonate. Preferably, the sodium perchlorate/calcium silicate compositions
20 include 15 to 25 percent of a water solution containing 60 to 75 wt% of sodium perchlorate monohydrate, 35 to 45 percent by weight calcium silicate and 30 to 50 percent by weight calcium carbonate. Free flowing powder compositions have been prepared by combining 15 percent by weight of 60 to 75 percent aqueous sodium perchlorate monohydrate and 40 percent calcium silicate and 45 percent calcium carbonate.

As noted, in practice, the sodium perchlorate/calcium silicate compositions are utilized in combination with a conventional heat stabilizer. In this regard, in accordance with the reduced hazard level aspect of the present invention, care should be exercised by the user to avoid potentially dangerous situations such as combining or otherwise contacting the perchlorate compositions with readily oxidizable compositions. Accordingly, from a reduced hazard level aspect, conventional stabilizers susceptible to ready oxidation such as organic phosphites are not recommended for use with perchlorate compositions. The amount of the sodium perchlorate/calcium silicate composition used in the
25 present invention is more preferably from 0.5 to 5 parts by weight of the weight of the polyvinyl chloride resin.

The stabilizer systems of the invention including conventional heat stabilizers and sodium perchlorate/calcium silicate long term heat stabilizers can be compounded with polyvinyl chloride resins, properly formulated, and shaped by standard plastics processing techniques involving processing temperatures in the range 150-205°C including calendering, extrusion, injection and compression molding, blow molding, rotational molding, slush and dip molding, solution casting, electrostatic spray and fluidized bed coating), to form a wide variety of motor vehicle components for both interior and exterior use, such as dashboards, seat coverings, floor mats, door panels, arm and headrests, receptacles, compartments, bodyside moldings, window trim moldings, seat comers and headliners, door and window knobs and crash dashboards.
35

Compounding components such as plasticizers, lubricants, impact modifiers, processing aids, fillers, colorants, antistatic agents, tackifiers, flame retardants, fungicides and antiblocking agents can be incorporated to facilitate the processing of such motor vehicle components.
40

The following examples demonstrate the usefulness of the present invention.

45 EXAMPLES 1-8

Polyvinyl chloride resin compositions were prepared having the following base formulation:

INGREDIENT	PARTS BY WEIGHT
50 Polyvinyl chloride homopolymer (OXY B-282)	100.0
Diundecyl Phthalate (Exxon)	40.0
Diisodecyl Phthalate (Exxon)	15.00
Epoxidized Soy Bean Oil (Drapex 6.8)	7.0
55 Primary Heat Processing Stabilizer (composition of approximately 60% weight percent barium stearate, 10 weight percent zinc laurate, 10 weight percent di-trimethylolpropane, 10 weight percent dibenzoylmethane, 8 weight percent calcium carbonate, and 2 weight percent 1,1,3-tris(2-methyl-4-hydroxy-5-1-butylphenyl) butane)	2.5

Depending upon the example, the following components were added to the base formulation:

EXAMPLE	PARTS BY WEIGHT ADDITION TO BASE FORMULATION
1*	None
2*	0.1 parts calcium silicate (Hubersorb 600)
3*	0.3 parts calcium silicate (Hubersorb 600)
4*	0.5 parts calcium silicate (Hubersorb 600)
5*	0.1 parts 60% NaClO ₄ aqueous solution (Kerr-McGee)
6*	0.2 parts 60% NaClO ₄ aqueous solution (Kerr-McGee)
7	0.3 parts calcium silicate (Hubersorb 600) 0.1 parts 60% NaClO ₄ aqueous solution (Kerr-McGee)
8	0.5 parts calcium silicate (Hubersorb 600) 0.2 parts 60% NaClO ₄ aqueous solution (Kerr-McGee)

* Comparative

The formulations of Examples 1-8, were blended on a two-roll mill, and then sheeted off.

To determine heat processing stability, samples of Examples 1-8 were cut from the sheets and heated in an oven at 177°C (350°F) and at 190°C (375°F) for up to two hours. Samples were withdrawn at fifteen minute intervals to follow the progress of any deterioration, as evidenced by visual discoloration and/or embrittlement.

The samples of Examples 1-8 were tested for long term heat stability at moderate temperatures. Samples of Examples 1-8 were placed in contact with foamed polyurethane and exposed at 121°C (250°F) in an oven for up to nineteen days. Samples were withdrawn at daily intervals and visually examined. Samples of Examples 1-8 were also placed on glass plates and exposed at 121°C (250°F) in an oven for up to seventeen days. Samples were withdrawn at daily intervals and visually examined.

The samples of Examples 1-8 subjected to the oven test at 177°C (350°F) showed relatively little visible difference throughout the test. At 190°C (375°F), samples from Examples 1-8 showed relatively little visible difference through thirty minutes. At forty minutes, samples from Examples 5 and 6 were visibly worse, i.e. had dark spots, than were samples from Examples 1-4 and 7-8. At fifty minutes, Examples 1, 2, 5 and 6 were visibly degraded, i.e. black; Examples 3 and 7 had dark spots like Examples 5 and 6 at forty minutes; Examples 4 and 8 had little or no degradation and were noticeably better than Examples 5 and 6 were at forty minutes. Sixty minute samples for Examples 1, 3, 4 and 8 were all badly discolored.

In the long term heat stability test wherein the polyvinyl was in contact with foamed polyurethane distinct visible differences were discernable between the control formulations, Examples 1-6, and the formulations illustrating the present invention, Examples 7-8. Base formula control Example 1 and control Example 2 containing added calcium silicate were visibly quite badly discolored by the seventh day. Control Examples 3 and 4 containing added calcium silicate performed at best marginally better than Example 1, and with each of Examples 3 and 4 being discolored by the ninth day to at least the same extent as were Examples 1 and 2 on day seven. Control Examples 5 and 6 containing added sodium perchlorate performed better than did Examples 1-4 at all comparable times through day nine. Example 5 was visibly quite badly discolored by the tenth day. By the tenth day Example 6 was somewhat better than was Example 5 but by day eleven Example 6 was visibly worse than Example 5 had been at day ten. In contrast, Examples 7 and 8, illustrating the present invention demonstrated as good if not better color through day eleven than did Examples 1-6. Furthermore, Example 7 although starting to display discernable discoloration at day twelve did not appreciably worsen from day twelve through eighteen. Example 8 performed better than did Example 7 and at day eighteen Example 8 was, at least as good if not: better than Examples 1 and 2 had been at day seven; better than Examples 3 and 4 had been at day nine; and better than Examples 5 and 6 had been at day ten.

The results of the long term heat stability without polyurethane present, were similar to the long term heat stability test in contact with polyurethane noted above for Examples 1-8. In general, added calcium silicate alone, i.e. Examples 2-4, performed worse than the base formula control, i.e. Example 1; added sodium perchlorate alone, i.e. Examples 5-6 is modestly helpful; and the present invention, i.e. Examples 7-8, is outstandingly better than the controls.

EXAMPLES 9-13

Polyvinyl chloride resin compositions were prepared having the following base formulation:

EP 0 457 471 B1

INGREDIENT	PARTS BY WEIGHT
Polyvinyl chloride homopolymer (GEON® 103)	100.0
Acrylic Modifier (Acryloid K175)	1.0

INGREDIENT	PARTS BY WEIGHT
Acrylic Modifier (Acryloid K125)	0.4
Acrylic Impact Modifier (KM-323B)	1.2
Ethylene bis stearamide lubricant	1.0
Titanium Dioxide	10.0
Calcium Stearate	1.2
Primary Heat Processing Stabilizer (methyltin isooctylthioglycolate mixture of approximately 20% monomethyltin tris isooctylthioglycolate and 80% dimethyltin bis isooctylthioglycolate)	1.5

Depending on the examples the following components were added to the base formulation:

EXAMPLE	PARTS BY WEIGHT ADDITION TO BASE FORMULATION
9	None
10	1.5 parts of a composition comprising 40% weight percent calcium silicate (Hubersorb 600), 45 weight percent calcium carbonate (Atomite) and 15 weight percent of 60% aqueous NaClO ₄ solution monohydrate (Kerr-McGee)
11	1.5 parts calcium silicate (Hubersorb 600)
12	1.5 parts of a composition comprising 55 weight percent calcium silicate (Hubersorb 600) and 45 weight percent calcium carbonate (Atomite)
13	1.5 parts of a composition comprising 45 weight percent calcium carbonate and 55 weight percent of 60% aqueous NaClO ₄ solution (Kerr-McGee)

EXAMPLES 14-18

Polyvinyl chloride resin compositions were prepared having the same base formulation as that used for Examples 9-13 except that the acrylic impact modifier (KM 323B) was present in 7 parts instead of 1.2 parts.

Depending on the example the following components were added to the base formulation:

EXAMPLE	PARTS BY WEIGHT ADDITION TO BASE FORMULATION
14	None
15	1.5 parts of a composition comprising 40% weight percent calcium silicate (Hubersorb 600), 45 weight percent calcium carbonate (Atomite) and 15 weight percent of 60% aqueous NaClO ₄ solution (Kerr-McGee)

EXAMPLE	PARTS BY WEIGHT ADDITION TO BASE FORMULATION
16	3.0 parts of a composition comprising 40% weight percent calcium silicate (Hubersorb 600), 45 weight percent calcium carbonate (Atomite) and 15 weight percent of 60% aqueous NaClO ₄ solution (Kerr-McGee)
17	1.5 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent tetra sodium pyrophosphate and 15 weight percent of 60% aqueous NaClO ₄ solution
18	1.5 parts of a tetra sodium pyrophosphate

EXAMPLES 19-24

Polyvinyl chloride resin compositions were prepared having the same base formulation as that used for Examples

9-13.

Depending on the example the following compounds were added to the base formulation:

EXAMPLE	PARTS BY WEIGHT ADDITION TO BASE FORMULATION
19	None
20	0.5 parts of a composition comprising 40% weight percent calcium silicate (Hubersorb 600), 45 weight percent calcium carbonate (Atomite) and 15 weight percent of 60% aqueous NaClO ₄ solution (Kerr-McGee)
21	1.5 parts of a composition comprising 40% weight percent calcium silicate (Hubersorb 600), 45 weight percent calcium carbonate (Atomite) and 15 weight percent of 60% aqueous NaClO ₄ solution (Kerr-McGee)
22	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent calcium carbonate and 15 weight percent of 60% aqueous NaClO ₄ solution (Kerr-McGee)
23	1.5 parts of a composition comprising 40 weight percent calcium silicate, 35 weight percent calcium carbonate, and 25 weight percent of 60% aqueous NaClO ₄ solution
24	1.5 parts calcium carbonate (Atomite)

The formulations of Examples 9-13, Examples 14-18, and Examples 19-24 were tested for stability under dynamic shear conditions by masticating at 60 rpm in the bowl of a Brabender Plastograph kept at 190°C a 60g quantity of each composition. After three minutes mastication, and subsequently at three minute intervals through 27 minutes and at 5 minute intervals thereafter, small samples of the composition were removed from the mixing bowl, pressed into a dime-sized button in a hand mold, and affixed to a record card.

Within each set of Examples, the results were visually examined to follow the progress of any deterioration, as evidenced by discoloration.

Degradation of Example 9, the base formulation, occurred at 32 minutes. Example 10, representing the present invention, extended the stable process time before degradation of Example 9 from 32 minutes to over 42 minutes with no sacrifice in early color content. Example 11, a control composition containing added calcium silicate only and Example 12, a control composition containing added calcium silicate and the inert of diluent calcium carbonate, each began noticeable degradation by 32 minutes, and at 37 minutes had visibly degraded to about the same extent as Example 9 had at 32 minutes. Example 13, a control composition containing added sodium perchlorate monohydrate with the inert diluent calcium carbonate at 37 minutes had visibly degraded to at least the same extent as Example 10 did at 42 minutes. Thus, none of the control compositions, Examples 11, 12 or 13, lasts as long as the present invention, Example 10, even though the total amount of additives is the same in each case.

The results of Examples 15, 16 and 17 (each representing the present invention) when compared to the results of the base formulation control, Example 14, and the added tetra sodium pyrophosphate control, Example 18, indicate the present invention relatively extends the stable process time before degradation without sacrificing early color. In particular, Example 14 reflects visible degradation at 27 minutes and substantial degradation at 32 minutes. Example 15 reflects visible degradation at 32 minutes and 37 minutes but noticeably less than that shown by Example 14 at 32 minutes. Example 18 demonstrates better performance than that for Example 14 but not as good as that for Example 15. Comparing different variations of the present invention, Example 17 demonstrates better performance, i.e. lesser visible degradation at respective times, than that for Example 15 but not as good as that for Example 16.

Degradation of Example 19, the base formulation, occurred at 32 minutes. Example 24, the control formulation containing calcium carbonate, reflected hardly different visual results from those of Example 19. Each of Examples 20-23, representing the present invention, extended the stable process time before degradation of Examples 19 and 24, without sacrificing early color. Particularly, Example 20 appeared less degraded at 37 minutes than did Example 19 at 32 minutes; Example 21 appeared visibly degraded at 37 minutes and 42 minutes but even at 42 minutes the degree of degradation appeared to be no more than that for Example 19 at 32 minutes; Example 22 did not appear to be visibly degraded until 42 minutes and at 42 minutes the degree of degradation appeared to be similar to that of Example 21 at 37 minutes; Example 23 appeared to provide very similar results as that for Example 22.

EXAMPLES 25-31

Polyvinyl chloride resin compositions were prepared having the following base formulations:

EP 0 457 471 B1

INGREDIENT	PARTS BY WEIGHT
Polyvinyl chloride homopolymer (OXY B-282)	100.0
Diundecyl Phthalate (Exxon)	40.0
Diisodecyl Phthalate (Exxon)	15.00
Epoxidized Soy Bean Oil (Drapex 6.8)	7.0
Calcium carbonate	10.0
Stearic acid	0.2
Primary Heat Processing Stabilizer (composition comprising 60% barium stearate, 10 weight percent zinc laurate, 5 weight percent dibenzoylmethane, 5 weight percent 4,4'-isopropylidenediphenol, and 20 weight percent dry Kaolin diluent)	2.0

Depending upon the example, the following components were added to the base formulation:

EXAMPLE	PARTS BY WEIGHT ADDITION TO BASE FORMULATION
25	None
26	0.6 parts composition comprising a 5 to 1 by weight blend of calcium silicate (Hubersorb 600) and 60% aqueous NaClO ₄ solution (Kerr-McGee)
27	1.2 parts composition comprising a 5 to 1 by weight blend of calcium silicate (Hubersorb 600) and 60% aqueous NaClO ₄ solution (Kerr-McGee)
28	0.5 parts calcium silicate

EXAMPLE	PARTS BY WEIGHT ADDITION TO BASE FORMULATION
29	1.0 parts calcium silicate
30	0.1 parts 60% aqueous NaClO ₄ solution
31	0.2 parts 60% aqueous NaClO ₄ solution

EXAMPLES 32-38

Polyvinyl chloride resin composition were prepared having the following base formulations:

INGREDIENT	PARTS BY WEIGHT
Polyvinyl chloride homopolymer (OXY B-282)	100.0
Diundecyl Phthalate (Exxon)	40.0
Diisodecyl Phthalate (Exxon)	15.00
Epoxidized Soy Bean Oil (Drapex 6.8)	7.0
Stearic acid	0.25
Calcium carbonate (Atomite)	10.0

Depending upon the example, the following components were added to the base formulation:

<u>EXAMPLE</u>	<u>PARTS BY WEIGHT ADDITION TO BASE FORMULATION</u>
32	None
33	0.2 parts 60% aqueous NaClO_4 solution
34	1.0 parts 60% aqueous NaClO_4 solution
35	0.2 parts 60% aqueous NaClO_4
<u>EXAMPLE</u>	<u>PARTS BY WEIGHT ADDITION TO BASE FORMULATION</u>
	solution
	0.5 parts calcium silicate (Hubersorb 600)
36	0.6 parts calcium silicate (Hubersorb 600)
37	1.0 parts of a composition comprising 40 weight percent calcium silicate (Hubersorb 600), 45 weight percent calcium carbonate (Atomite) and 15 weight percent of 60% aqueous NaClO_4 solution (Kerr-McGee)
38	1.0 parts of a composition comprising 40 weight percent calcium silicate (Hubersorb 600), 35 weight percent calcium carbonate (Atomite) and 25 weight percent of 60% aqueous NaClO_4 solution (Kerr-McGee)

The formulations of Examples 25-31 and Examples 32-38 were blended on a two-roll mill, and then sheeted off.

To determine the heat processing stability, samples were cut from sheets and heated in an oven at 177°C (350°F) for up to two hours and at 190°C (375°F) for up to 80 minutes. Samples were withdrawn at fifteen minute intervals at 177°C (350°F) and at ten minute intervals at 190°C (375°F) to follow the progress of any deterioration, as evidenced by visual discoloration and/or embrittlement.

Comparing within Examples 25-31, the compositions of the present invention, i.e. Examples 26 and 27, to the base control formulation, i.e. Example 25, and the comparison control formulations, i.e. Examples 28-31, the samples of Examples 26 and 27 are less discolored off the mill and throughout the oven test than are the respective time samples from Examples 25 and 28-31.

The base formulation for Examples 32-38 contains epoxidized soy bean oil as the only base stabilizing additive. Examples 35, 37 and 38 illustrate the present invention. Example 32 represents the base formulation control and

Examples 33, 34 and 36 represent controls containing sodium perchlorate or calcium silicate as identified above. Samples from control Examples 32 and 36 were slightly discolored to an undesirable pink off the mill (time zero). Samples from Examples 35, 37 and 38 were clean off the mill (time zero) and resisted degradation to brown (a sign of objectionable cross linking) until the 60 or 75 minute chip at 177°C (350°F) and the 30 or 40 minute chip at 190°C (375°F).
 5 Samples from control Examples 33 and 34 were also clean off the mill (time zero) but degraded to brown by the 45 minute chip at 177°C (359°F) and by the 20 minute chip at 190°C (375°F).

Claims

- 10 1. A vinyl halide composition of improved stability at moderate aging temperatures which comprises a polyvinyl chloride resin, and an effective amount of a primary heat stabilizer composition to provide processing stability at processing temperatures of 150°C (300°F) to 205°C (400°F), and 0.1 to 10 parts by weight based on the weight of the polyvinyl chloride resin of a secondary heat stabilizer composition including sodium perchlorate hydrate and
 15 calcium silicate.
2. The composition according to claim 1 wherein said primary heat stabilizer is an organotin stabilizer or metal salt stabilizer.
- 20 3. The composition according to claim 2 wherein the organotin stabilizer is an organotin mercaptide, organotin sulfide, organotin carboxylate or a mixture thereof.
4. The composition according to claim 2 wherein the metal salt stabilizer is a barium salt, zinc salt or a mixture thereof.
- 25 5. The composition according to any one of claims 1 to 4 wherein the secondary stabilizer composition further includes a non-absorbing diluent powder.
6. The composition according to claim 5 wherein said diluent powder is calcium carbonate, a zeolite, silica, alumina, a PVC resin, barium sulfate or a mixture thereof.
- 30 7. The composition according to claim 6 wherein said secondary stabilizer composition includes 30 to 50 weight percent of calcium silicate, 30 to 50 weight percent of calcium carbonate, and 10 to 30 weight percent of a water solution containing 60 to 75 weight percent of sodium perchlorate monohydrate.
- 35 8. The composition according to claim 7 wherein the secondary stabilizer composition includes 35 to 45 weight percent of calcium silicate, 30 to 50 weight percent of calcium carbonate, and 15 to 25 weight percent of a water solution containing 60 to 75 weight percent of sodium perchlorate monohydrate.
- 40 9. The composition according to claim 8 wherein said secondary stabilizer composition includes 40 weight percent of calcium silicate, 45 weight percent of calcium carbonate, and 15 weight percent of a water solution containing 60 to 75 weight percent of sodium perchlorate monohydrate.
- 45 10. The composition according to any one of the preceding claims wherein the secondary heat stabilizer composition is present in an amount of 0.5 to 5 parts by weight based on the weight of the polyvinyl chloride resin.
11. A motor vehicle component having an improved stability at moderate temperatures, comprised of a shaped vinyl halide composition according to any one of the preceding claims.
- 50 12. A process for preparing a motor vehicle component having an improved stability at moderate temperatures which comprises forming a vinyl chloride resin composition according to any one of claims 1 to 10 at a heat processing temperature within the range from 150°C to 205°C (300°F to 400°F) in the selected shape.
13. A free flowing powder perchlorate stabilizer composition of reduced hazard level comprising sodium perchlorate hydrate, calcium silicate, and a non-absorbing inert diluent powder.
- 55 14. The stabilizer composition according to claim 13 wherein said diluent is calcium carbonate.
15. The composition according to claim 13 or claim 14 wherein the secondary stabilizer composition is as defined in

any one of claims 5 to 10.

Patentansprüche

5

10

15

20

25

30

35

40

45

50

55

1. Vinylhalogenid-Zusammensetzung mit verbesserter Stabilität bei mäßigen Alterungstemperaturen, umfassend ein Polyvinylchloridharz und eine wirksame Menge einer primären Wärmestabilisator-Zusammensetzung, um bei Verarbeitungstemperaturen von 150°C (300°F) bis 205°C (400°F) für Verarbeitungsstabilität zu sorgen, sowie 0,1 bis 10 Gewichtsteile, bezogen auf das Gewicht des Polyvinylchloridharzes, einer sekundären Wärmestabilisator-Zusammensetzung, umfassend Natriumperchlorat-hydrat und Kalziumsilikat.
2. Zusammensetzung nach Anspruch 1, worin der primäre Wärmestabilisator ein Organozinn-Stabilisator oder ein Metallsalz-Stabilisator ist.
3. Zusammensetzung nach Anspruch 2, worin der Organozinn-Stabilisator ein Organozinmercaptid, Organozinn-sulfid, Organozinncarboxylat oder ein Gemisch davon ist.
4. Zusammensetzung nach Anspruch 2, worin der Metallsalz-Stabilisator ein Bariumsalz, ein Zinksalz oder ein Gemisch davon ist.
5. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin die sekundäre Stabilisator-Zusammensetzung weiters ein nichtabsorbierendes Verdünnerpulver umfaßt.
6. Zusammensetzung nach Anspruch 5, worin das Verdünnerpulver Kalziumcarbonat, ein Zeolith, Kieselsäure, Aluminiumoxid, ein PVC-Harz, Bariumsulfat oder ein Gemisch davon ist.
7. Zusammensetzung nach Anspruch 6, worin die sekundäre Stabilisatorzusammensetzung 30 bis 50 Gew.-% Kalziumsilikat, 30 bis 50 Gew.-% Kalziumcarbonat und 10 bis 30 Gew.-% einer wäßrigen Lösung enthält, die 60 bis 75 Gew.-% Natriumperchlorat-monohydrat enthält.
8. Zusammensetzung nach Anspruch 7, worin die sekundäre Stabilisator-Zusammensetzung 35 bis 45 Gew.-% Kalziumsilikat, 30 bis 50 Gew.-% Kalziumcarbonat und 15 bis 25 Gew.-% einer wäßrigen Lösung enthält, die 60 bis 75 Gew.-% Natriumperchlorat-monohydrat enthält.
9. Zusammensetzung nach Anspruch 8, worin die sekundäre Stabilisator-Zusammensetzung 40 Gew.-% Kalziumsilikat, 45 Gew.-% Kalziumcarbonat und 15 Gew.-% einer wäßrigen Lösung enthält, die 60 bis 75 Gew.-% Natriumperchloratmonohydrat enthält.
10. Zusammensetzung nach einem der vorhergehenden Ansprüche, worin die sekundäre Wärmestabilisator-Zusammensetzung in einer Menge von 0,5 bis 5 Gewichtsteilen, bezogen auf das Gewicht des Polyvinylchloridharzes, vorhanden ist.
11. Kraftfahrzeugkomponente mit verbesserter Stabilität bei mäßigen Temperaturen, bestehend aus einer geformten Vinylhalogenid-Zusammensetzung nach einem der vorhergehenden Ansprüche.
12. Verfahren zur Herstellung einer Kraftfahrzeugkomponente mit verbesserter Stabilität bei mäßigen Temperaturen, umfassend das Formen einer Vinylchloridharz-Zusammensetzung nach einem der Ansprüche 1 bis 10 bei einer Warmverarbeitungstemperatur im Bereich von 150°C bis 205°C (300° bis 400°F) in die gewählte Form.
13. Frei fließende, pulverförmige Perchlorat-Stabilisatorzusammensetzung mit herabgesetztem Gefahrenpotential, umfassend Natriumperchlorat-hydrat, Kalziumsilikat und ein nichtabsorbierendes, inertes Verdünnerpulver.
14. Stabilisatorzusammensetzung nach Anspruch 13, worin der Verdünner Kalziumcarbonat ist.
15. Zusammensetzung nach Anspruch 13 oder 14, worin die sekundäre Stabilisatorzusammensetzung wie in einem der Ansprüche 5 bis 10 definiert ist.

Revendications

- 5 1. Composition d'halogénure de vinyle ayant une meilleure stabilité à des températures modérées de vieillissement qui comprend une résine de chlorure de polyvinyle et une quantité efficace d'une composition d'un stabilisant primaire à la chaleur pour donner une stabilité au traitement à des températures de traitement de 150°C (300° F) à 205°C (400°F) et 0,1 à 10 parties en poids, en se basant sur le poids de la résine de chlorure de polyvinyle, d'une composition d'un stabilisant secondaire à la chaleur comprenant du perchlorate de sodium hydraté et du silicate de calcium.
- 10 2. Composition selon la revendication 1 où ledit stabilisant primaire à la chaleur est un stabilisant d'organo-étain ou un stabilisant d'un sel métallique.
- 15 3. Composition selon la revendication 2 où le stabilisant d'organo-étain est un mercaptide d'organo-étain, un sulfure d'organo-étain, un carboxylate d'organo-étain ou un mélange.
- 20 4. Composition selon la revendication 2 où le stabilisant d'un sel métallique est un sel de baryum, un sel de zinc ou un mélange.
- 25 5. Composition selon l'une quelconque des revendications 1 à 4 où la composition du stabilisant secondaire contient de plus une poudre d'un diluant non absorbant.
- 30 6. Composition selon la revendication 5 où ladite poudre d'un diluant est le carbonate de calcium, une zéolite, de la silice, de l'alumine, une résine PVC, du sulfate de baryum ou un mélange.
- 35 7. Composition selon la revendication 6 où ladite composition du stabilisant secondaire contient 30 à 50 % en poids de silicate de calcium, 30 à 50 % en poids de carbonate de calcium et 10 à 30 % en poids d'une solution dans l'eau contenant 60 à 75 % en poids de perchlorate de sodium monohydraté.
- 40 8. Composition selon la revendication 7 où la composition du stabilisant secondaire contient 35 à 45 % en poids de silicate de calcium, 30 à 50 % en poids de carbonate de calcium et 15 à 25 % en poids d'une solution dans l'eau contenant 60 à 75 % en poids de perchlorate de sodium monohydraté.
- 45 9. Composition selon la revendication 8 où ladite composition du stabilisant secondaire contient 40 % en poids de silicate de calcium, 45 % en poids de carbonate de calcium et 15 % en poids d'une solution dans l'eau contenant 60 à 75 % en poids de perchlorate de sodium monohydraté.
- 50 10. Composition selon l'une quelconque des revendications précédentes où la composition du stabilisant secondaire à la chaleur est présente en une quantité de 0,5 à 5 parties en poids en se basant sur le poids de la résine de chlorure de polyvinyle.
- 55 11. Composant pour véhicule à moteur ayant une meilleure stabilité aux températures modérées composé d'une composition d'halogénure de vinyle en forme selon l'une quelconque des revendications précédentes.
12. Procédé de préparation d'un composant d'un véhicule à moteur ayant une meilleure stabilité aux températures modérées, qui consiste à former une composition de résine de chlorure de polyvinyle selon l'une quelconque des revendications 1 à 10 à une température de traitement thermique entre 150°C et 205°C (300°F à 400°F) dans la forme sélectionnée.
13. Composition d'un stabilisant de perchlorate en poudre fluide d'un niveau réduit de danger comprenant du perchlorate de sodium hydraté, du silicate de calcium et une poudre d'un diluant inerte non absorbant.
14. Composition d'un stabilisant selon la revendication 13 où ledit diluant est le carbonate de calcium.
15. Composition selon la revendication 13 ou la revendication 14 où la composition du stabilisant secondaire est telle que définie selon l'une quelconque des revendications 5 à 10.